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Transport of $Zn(OH)_4^{2-}$ ions across a polyolefin microporous membrane

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Abstract

Transport of $Zn(OH)_4^{2-}$ ions through modified microporous polypropylene membranes (Celgard 3401, 3501) was studied using polarography and conductometry. Soluble Nafion as an ion exchange modifying agent was applied to the membrane by several techniques. The influence of Nafion and a surfactant on transport of zinc ions through the membrane was studied. A relationship between membrane impedance and the rate of $Zn(OH)_4^{2-}$ transport was found. The found correlation between conductivity, ion permeability and Nafion coverage suggests a suitable technique of membrane preparation to obtain desired zinc ion barrier properties.

Although primary cells with zinc electrodes are widespread, secondary systems based on the same materials still suffer from a short life time arising from problems caused by zinc mass redistribution, undesirable changes in zinc morphology and the influence of zinc ions on the opposite electrodes. Because nickel–zinc and manganese dioxide–zinc systems are otherwise suitable for electric vehicle propulsion, an effort to develop a long–lasting storage battery is very desirable. One avenue is to find a better electrode separator for such systems.

A separator in an accumulator with a zinc electrode has a dual specific role – to provide a mechanical barrier to the growth of zinc dendrites and to protect the cathode active material from diffusing $Zn(OH)_4^{2-}$ ions that can influence its ability to be charged.

Many different types of separators were under investigation in the past (1). The best results were achieved with microporous separators (2–4) and ion–exchange membrane separators (5–7). Microporous separators show slower redistribution of Zn material compared to ion–exchange membranes, but they have less favorable zinc exclusion selectivity. In this work, an attempt is made to merge the good attributes and to avoid some of the disadvantages of the two types of separators and to prepare a composite separator with slow redistribution of zinc material, better ion exclusion and good conductivity. Polypropylene membranes were chosen as suitable microporous separators which were then coated with Nafion to afford increased ionic selectivity.

Experimental

A special cell suitable both for membrane impedance measurements and for determination of the amount of transported Zn ions, without intervening with the membrane, was designed. The cell, based on the EG&G polarographic cell, allows simple manipulation of different membranes, application of electric field during ion transport, and using of inert atmosphere. The part of the cell with the membrane mounted on its bottom

(*1*, Fig. 1 and 2) is common for both the ion transport and membrane resistance measurements. Its volume is 40 ml. Different cell containers are used for the two types of measurements, as shown in Fig. 1 and 2.

Celgard 3401 and Celgard 3501 (Hoechst Celanese Corp., Charlotte, NC) microporous separators were chosen because they are proven to have slow redistribution of zinc material, good mechanical properties and good chemical resistivity. The name Celgard is a registered trade name of Hoechst Celanese. Typical reported porosities for Celgard 3401 and Celgard 3501 are 38 % and 45 % respectively, the pore dimensions are (width x length) 0.05 x 0.125 μm and 0.075 x 0.25 μm and thickness for both 25 ± 2.5 μm. The electrical resistance of the hydrophilic versions of the membranes measured by the Celanese procedure is 78 mΩ/cm^2 and 39 mΩ/cm^2, respectively, in 40 % KOH ($\simeq$ 10 mol/l).

These membranes are normally supplied in a hydrophilic form which is achieved by treatment with a cationic/nonionic surfactant. For the purpose of some of the experiments a hydrophobic membrane was prepared. The surfactant was removed by multiple washing in methanol of analytical grade.

The membranes were cut into a needed size before the modifying treatment. After the treatment, they were attached to the cell either by wrapping with a teflon tape or by tightening under a special hollow nut. The exposed area of the membrane was 2.2 cm^2.

The membrane modifying material was a solution of cation exchange polymer prepared from Nafion 117 membrane (E. I. DuPont de Nemours & Co., USA, Nafion is a registered trademark). It was either a 5 % Nafion solution in a mixture of lower aliphatic alcohols and 10 % water, commercially available from Aldrich, or an aqueous solution without alcohols, prepared according to Weber, Kavan and Štícha (8) from the Aldrich soluble Nafion. The Celgard membranes were coated with Nafion from its alcoholic or aqueous solutions of various concentrations using several techniques described in the result section. The amount of Nafion in the membrane was determined by weighing the difference of the treated and untreated membrane.

Fisher Certified A.C.S. chemicals and twice distilled water were used. KOH contained reported 0.0005 % of Fe and 0.0003 % of heavy metals (as Ag). ZnO contained 0.001 % of Pb and 0.0005 % of Fe. A 6 mol/l KOH solution was used in all experiments. $Zn(OH)_4^{2-}$ transport was studied on solutions of 0.1 mol/l ZnO dissolved in 6 mol/l KOH.

$Zn(OH)_4^{2-}$ transport across the membranes was determined polarographically, using a Princeton Applied Research Polarographic Analyzer Model 364 and a cell from Fig. 1. Hg/HgO immersed in 6 mol/l KOH and equipped with a Luggin capillary was the reference. A linear calibration curve was obtained from wave heights of standard $Zn(OH)_4^{2-}$ solutions in concentration range $0.2 - 10$ mmol/l. Zinc limiting current was read at -1.5 V vs. Hg/HgO, with a background current measured at -1.2 V subtracted.

Frequency dependent electrical impedance was studied using either a Solartron 1255 Frequency Response Analyser in conjunction with the 1286 Solartron Electrochemical Interface or a Hewlett-Packard Impedance Analyzer Model 4192A. The AC perturbation signal was in all cases 10 mV. All measurements were done on membranes soaked in respective solutions for a period of time so that a steady–state was achieved.

Results and discussion

Table I lists properties of membranes prepared by several procedures. Sample No. 1 is an original membrane with its native surfactant, and sample No. 2 is a membrane with its commercial surfactant removed. Further samples are membranes coated with Nafion from its alcoholic solutions at room temperature. Sample No. 5 was immersed in a mixture of 1 ml Nafion (5 % Nafion in alcoholic solution) diluted with 3 ml of propanol. Sample No. 4 was soaked in the same mixture, further diluted by additional 3 ml of propanol. Sample No. 3 was soaked in a Nafion solution with 6 more milliliters of propanol added.

The differences between commercial uncoated membranes in their hydrophilic form, hydrophobic form without the surfactant and the membranes coated with Nafion, were

studied by measuring the modulus of impedance ($|Z|$) and the phase shift (φ) for the membranes. The impedance values $|Z|$ for five different membranes measured at 50 kHz, where the phase shift is close to zero, are in Table I.

The surfactant coating on the commercially supplied membrane (sample No. 1) maintains its high conductivity, presumably due to wettability of the membrane and exclusion of trapped air. The frequency dependence of $|Z|$ and φ between 100 Hz – 1 MHz is not invariant which suggests a certain capacitive component of the membrane. The membrane No. 2 is without a surfactant and any other coating and it is effectively hydrophobic. Therefore it exhibits a higher $|Z|$ throughout the experimental range (100 Hz – 1 MHz). The phase shift φ is close to zero, which suggests that the membrane behaves as a resistor in an equivalent circuit.

Membrane Celgard 3501 coated with 0.024 mg/cm^2 of Nafion and without any surfactant (sample No. 3) had $|Z|$ slightly below 10 Ω/cm^2 and it was nearly constant throughout the experimental frequency range. The phase shift φ was close to zero. With increasing mass of Nafion deposited on the membrane (0.047 mg/cm^2 for No. 4), the value of $|Z|$ became smaller, in the range of 1.7 to 1.9 Ω/cm^2, with larger frequency dependence. Similarly, φ varied appreciably more than for sample No. 3, between zero and ten degrees. The frequency dependence and φ variation was even greater for sample No. 5 which had the largest deposited mass of Nafion. The phase shift was close to zero at frequencies around 50 kHz, a frequency that was chosen for comparison of all membranes.

Transport of the $Zn(OH)_4^{2-}$ ions through a Nafion coated membrane was studied by monitoring changes in zinc ion concentration inside the vessel 1 of Fig. 1. Since the inside solution was stirred, the polarographic response gave reliable information about the rate of zinc transport through the film. Zinc transport, driven by concentration gradient, was increasing with the increasing amount of Nafion deposited in the membrane. The flux of zinc transport and the impedance values for several Nafion treated membranes are summarized in Table I.

It is possible to estimate an apparent diffusion coefficient of zinc ions in the membrane from the fluxes listed in the last column of Table I. It holds that

$$D = - \frac{j}{\mathrm{grad}\ c} = - \frac{j\ \Delta x}{\Delta c}. \tag{1}$$

The membrane thickness Δx was 25×10^{-4} cm and the zinc ion concentration gradient between two baths at 0.0 mol/l and 0.1 mol/l was $\Delta c = - 1.0 \times 10^{-4}$ mol/cm^3. Thus the apparent diffusion coefficient for zinc in the membrane with 0.047 mg/cm^2 of Nafion was 1.14×10^{-8} cm^2 s^{-1} and in the membrane with 0.079 mg/cm^3 Nafion it was 8.55×10^{-8} cm^2 s^{-1}.

The commercial hydrophilic form of Celgard 3401 with a surfactant has maximum value of electrical resistance (specified by the manufacturer) 39 mΩ/cm^2 in 40 % KOH. The effect of the surfactant on the membrane impedance in the presence of Nafion coating is seen in Table II. Two membranes were made first hydrophobic by rinsing their surfactant off by alcohol. Then one of them was coated from alcoholic solution containing 1 % Nafion, whereas the second was coated in the same solution containing added surfactant. The coating was done in an ultrasonic bath.

For a membrane without the surfactant, coated in a 1 % solution of Nafion, no zinc ion transport was detected during a five–hour experiment. The impedance modulus at 50 kHz was quite high, 186 Ω. This resistance was probably caused by hydrophobization of the membrane. Although Nafion in excess on the membrane surface coats the membrane, the hydrophobic pores inside the membrane exclude Nafion and the pores, some of them likely filled with trapped air, render low conductivity and the membrane behaves more like a capacitor. Use of a surfactant, obtained from rinsing of a supply of new Celgard membranes, decreased the impedance modulus significantly to 330 mΩ. Similarly, an increase in zinc ion flux through the membrane was observed as shown in Table II. The surfactant increased the membrane conductivity, but at the expense of higher zinc ion transport, a property undesirable for a practical storage battery application.

Higher amounts of Nafion, coating the membrane, increase both the membrane

conductivity and its ability to allow zinc ions to pass. The majority charge carrier through Nafion in the case of KOH electrolyte are K^+ ions. Increased zinc concentration will increase zinc permeation, but since zinc ions are larger than K^+, the contribution of zinc to the conductivity increase is nevertheless small.

Figure 3 shows the correlation between impedance modulus recorded at 50 kHz and the membrane ability to pass zinc ions. The results include uncoated membranes as well as membranes coated in various ways, and they include both Celgard 3401 and 3501 data. The two types of membranes are not distinguishable in this graph, although the points left of $j=20x10^6$ mol cm^{-2} hr^{-1} mostly correspond to Celgard 3501. There are four groups of data points. The group of squares (□) represents values for commercial membranes in their hydrophilic form without any Nafion coating. These types of membranes with good conductivity are used in practice as electrode separators (2–4) although zinc flux is relatively high and it is further enhanced by charge flow during operation of the source. The group of crosses (x) arises from the same commercial membranes whose transport properties are modified by applied electric field. The region of the triangles (△) consists of responses by a group of membranes with a surfactant, coated by Nafion using several different procedures. The group of circles (o) represents the membranes coated with an excess of Nafion and mainly stripped of the surfactant.

Presence of Nafion in the membrane decreases its conductivity below the value for its untreated form, as well as it lowers the zinc transport driven by concentration gradient. This relationship is not, however, linear. The relationship of |Z| vs. flux of zinc ions falls, within some data spread, on the curve outlined in Fig. 3. The same curve can be constructed regardless of the method of Nafion application to the membrane. The location of the data on the curve predicts usefulness of a certain membrane to such applications as zinc electrolyte separation while maintaining its relatively high conductivity.

The section of triangles (△) is very promising for the power sources application although the treated membranes have higher resistance than membranes without any

treatment. The filled symbols (A, B, C, D, E) in Fig. 3 are experimental values for Celgard 3501 with conditions further specified in the legend for the figure and listed in Table I.

To understand the effects that electric field applied across the membrane may have on ion transport, a series of experiments was performed in which ion flux through the membrane was measured at a condition in which a steady current was applied across the membrane. Positive field increased zinc ion transport as expected, because in the basic solution zinc exists as an anion. The flux increase at applied current density of $5\,\mathrm{mA/cm}^2$ was about 10 % higher than flux maintained only by concentration gradient for either type (3401 and 3501) of the membrane. The flux/impedance results that correspond to that particular membrane with the flux enhanced by current flow are shown in Fig. 3 by crosses ($\times$). Similarly, a negative field, opposing the ion flow, decreased the flux of zinc.

Table III lists results obtained with a Celgard 3501 membrane which was impregnated by vacuum–suction of 5 ml (2 ml in the case of the 1 % solution) of an alcoholic Nafion solution of desired concentration through the membrane fastened to the polarographic cell. *Although the membrane was originally in its hydrophilic version, suction of excess methanol* (10 ml) *through it rinsed the surfactant off the membrane.* For comparison, the last membrane in Table III was additionally treated with surfactant.

Comparison of the first value from this table for Celgard 3501 and the result obtained with a Celgard 3401 membrane that was coated using the same Nafion solution in an ultrasonic bath (Tab. II) reveals that Celgard 3401, which has smaller pores and higher native resistance, produces actually more conductive membranes but with correspondingly higher value of zinc flux. The difference in conductivity is likely due to the porosity and pore size of the original membrane and the method of preparation has only a secondary effect.

Lowering Nafion concentration produces membranes with lower conductivity. This decrease is more pronounced with the suction technique as compared to the membranes obtained by immersion in ultrasonic bath. The suction method produces at low Nafion concentration membranes for which the measured zinc flux is zero, which is expected due to

the high overall resistivity. The decrease in conductivity can be explained by rinsing off the surfactant by the excess of methanol in the coating solution. The surfactant added to the preparatory solution significantly increased the conductivity but increased the zinc ion flux as well. The flux through the Nafion+surfactant membrane is about two thirds that of the original uncoated hydrophilic membrane.

A number of membranes was prepared using several different techniques of preparation. One technique was immersion in alcoholic or aqueous Nafion solution at room temperature (see text for Table 1). Another way was to impregnate the membrane at elevated temperature. It was boiled in a solution of Nafion and methanol (0.1 % of Nafion in the mixture) under a reflux condenser for approximately one hour, and allowed to cool either in the solution or in the air. This procedure did not generate coverages significantly different from those obtained by immersion in cold solutions. Yet another method used to impregnate the membranes was to immerse them in a mixture of Nafion and methanol under partial vacuum, in an ultrasonic bath or both. The expected purpose of this effort was to expel any gas trapped inside the membrane. A variation of this method was to apply vacuum suction on the membrane and express the Nafion solution of desired concentration through it.

In most cases the behavior of the treated membranes varied very little with the method of preparation. Their impedance shortly after immersion in 6 mol/l KOH was relatively very high (typically $1 - 15$ kΩ) while the phase angle was in tens of degrees and up to 90^0. The membrane behaved shortly after immersion mainly as a capacitor. After several minutes the impedance fell to $10 - 100$ Ω and the phase angle was typically below one degree indicating a pure resistive behavior. The measured impedance leveled off within 24 hours, but usually sooner.

The ultrasonic treatment or the suction method were the most successful in terms of obtaining a membrane with relatively high conductivity. By contrast, membranes treated by simple dipping in Nafion had higher resistance and long time was required after immersion into a solution for the electrical parameters to stabilize. Figure 4 shows time changes of

10

impedance for Celgard 3501 in a hydrophobic form as a response to immersion in 6 mol/l KOH. These membranes were previously coated by immersion in Nafion of several different concentrations. In comparison with Table III, that lists properties of membranes impregnated by suction, it is obvious that simple immersion in Nafion solution of the same concentration leaves the membrane with much higher resistance. Curve A and the first value in Table III correspond to the same Nafion stock solution concentration but the resistance of the dip–coated membrane is more that hundred times higher. It is likely that at this concentration Nafion covers the surface of the membrane, without significant penetration, and traps inside electrically insulating air. Curve B for lower Nafion concentration and corresponding higher conductivity is probably the result of lower surface concentration and deeper penetration of Nafion inside the membrane. Curves C and D which are the responses of progressively lower concentrations of Nafion exhibit high resistances, comparable to those obtained with the suction method. In both cases, the amount of Nafion available for membrane modification is too low and the membranes remain largely uncoated and with some surfactant washed away by the alcoholic solution.

The time dependence observed in Fig. 4 shows that the lower and a steady state resistance of the membranes is reached after about 2 hour immersion in the bathing electrolyte. From that time on the resistance values remain virtually constant over a period of several days, which indicates that the applied Nafion modifier is durable. The results reported in this work were obtained on membranes immersed at least for 1 hour in a bathing solution to attain a steady state.

Conclusions

It has been shown in this work that the combination of the ionomer amount and the method how it is applied to the membrane is a possible way how to modify the desired attributes of microporous membranes. Nafion as an ion exchange polymer has been used in

this work as a modifier influencing selectivity and flow of $Zn(OH)_4^{2-}$ ions. The study of Nafion trapped in membrane pores is particularly important for better understanding of microheterogeneous systems where the intricate channels of Nafion are of interest. A significant role of the surfactant in its combination with an ionomer has been shown. Inverse dependence of membrane conductivity and the flux of the $Zn(OH)_4^{2-}$ ions through the microporous membrane, experimentally obtained from work with variously modified membranes, reveals that a very fine balance of several factors (type and amount of the ionomer, its spatial distribution in the microporous membrane, kind, presence and quantity of the surfactant and the presence of the electric field) account for the ion selective membranes with high conductivity. The method of application of Nafion to the membrane by the suction or sonication techniques is to be preferred if membranes with high conductivities are desired. By adjusting the parameters and procedures of coating, a membrane with optimized resistance and ion exclusion properties can be prepared.

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Legend for figures:

Fig. 1.　Membrane holder in the arrangement for polarographic measurement of transport of $Zn(OH)_4^{2-}$ ions across the membrane. 1 – polarographic vessel, 2 – bottom container (on a magnetic stirrer, with a stir–bar inside), 3 – membrane, 4 – mercury collector, 5 – 6 mol/l KOH with 0.1 mol/l ZnO, 6 – 6 mol/l KOH, 7 – mechanical stirrer, CE – counter electrode, RE – reference electrode, MDE – mercury dropping electrode, (Aux) – auxiliary electrode separated by a frit, used in current flow measurements, N_2 – nitrogen gas inlets.

Fig. 2.　Membrane holder in the arrangement for impedance measurements. 1 – polarographic vessel identical to the one in Fig. 1., 2 – lid with electrodes, 3 – bottom container with electrodes, 4, 5 – potential electrodes, 6, 7 – current electrodes, 8 – membrane.

Fig. 3.　*Relationship between the absolute impedance modulus measured at 50 kHz and zinc flux across Celgard 3401 and 3501 membranes treated in several ways. Areas (o) and (Δ) are Nafion coated membranes (o – without surfactant, Δ – with surfactant). More conductive uncoated membranes are in region (□) and in region (ɪ) which is the same membrane with transport enhanced by applied electric field. The filled symbols are the values listed in the Tab. I. A – uncoated membrane with surfactant, B – 0.079 mg/cm^2 Nafion, C – 0.047 mg/cm^2 Nafion, D – 0.024 mg/cm^2 Nafion, E – uncoated membrane without surfactant.*

Fig. 4.　Time dependence of the impedance modulus measured at 50 kHz for a membrane Celgard 3501 (hydrophobic form) dip–coated in alcoholic solutions of Nafion of different concentrations. A(ɪ): c = 0.8 %, B(●): c = 0.1 %, C(Δ): c = 0.05 %, D(□): c = 0.025 % .

Tables:

Table I. Dependence of the flow of zinc through the membrane and its impedance modulus as a function of modifications of the membrane.

	Membrane Celgard 3501		
Sample No.	Nafion $[mg/cm^2]$	j $[10^{-6}$ mol cm^{-2} hr$^{-1}]$	$|Z|$ $[\Omega/cm^2]$ at 50 kHz
1	0 + surfactant	34.0	0.046
2	0 − no surfactant	0.0*	138
3	0.024	0.36	9.85
4	0.047	1.6	1.684
5	0.079	12.0	0.250

* None detected for first 5 hours

Table II. Zinc ion flux and absolute impedance of the Nafion coated membrane with and without surfactant. Coated with 1 % Nafion iu ultrasonic bath.

	Membrane Celgard 3401	
Surfactant [yes/no]	j $[10^{-6}$ mol cm^{-2} hr$^{-1}]$	$|Z|$ $[\Omega$ cm$^{-2}]$ at 50 kHz
no	0*	186.0
yes	16.4	0.330

* None detected for first 5 hours

Table III. Membranes prepared by the vacuum–suction method.

	Membrane Celgard 3501	
% of Nafion in the solution	j $[10^{-6}$ mol cm^{-2} hr$^{-1}]$	$|Z|$ $[\Omega$ cm$^{-2}]$ at 50 kHz
1.0	14.6	0.685
0.1	0	4.37
0.025	0	41.5
0.005	0	73.0
0.005 + surfactant	20.0	0.26

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N_2

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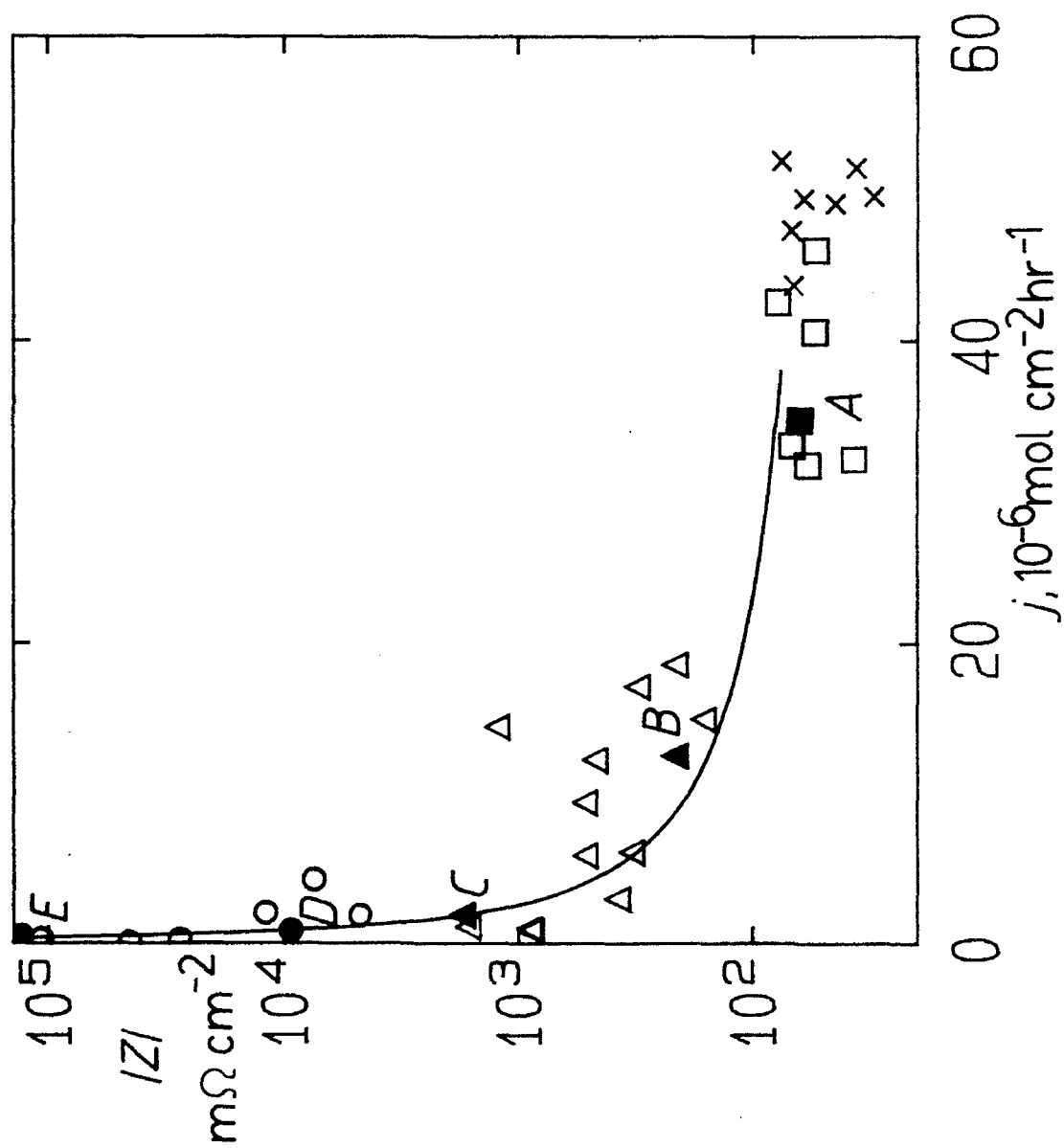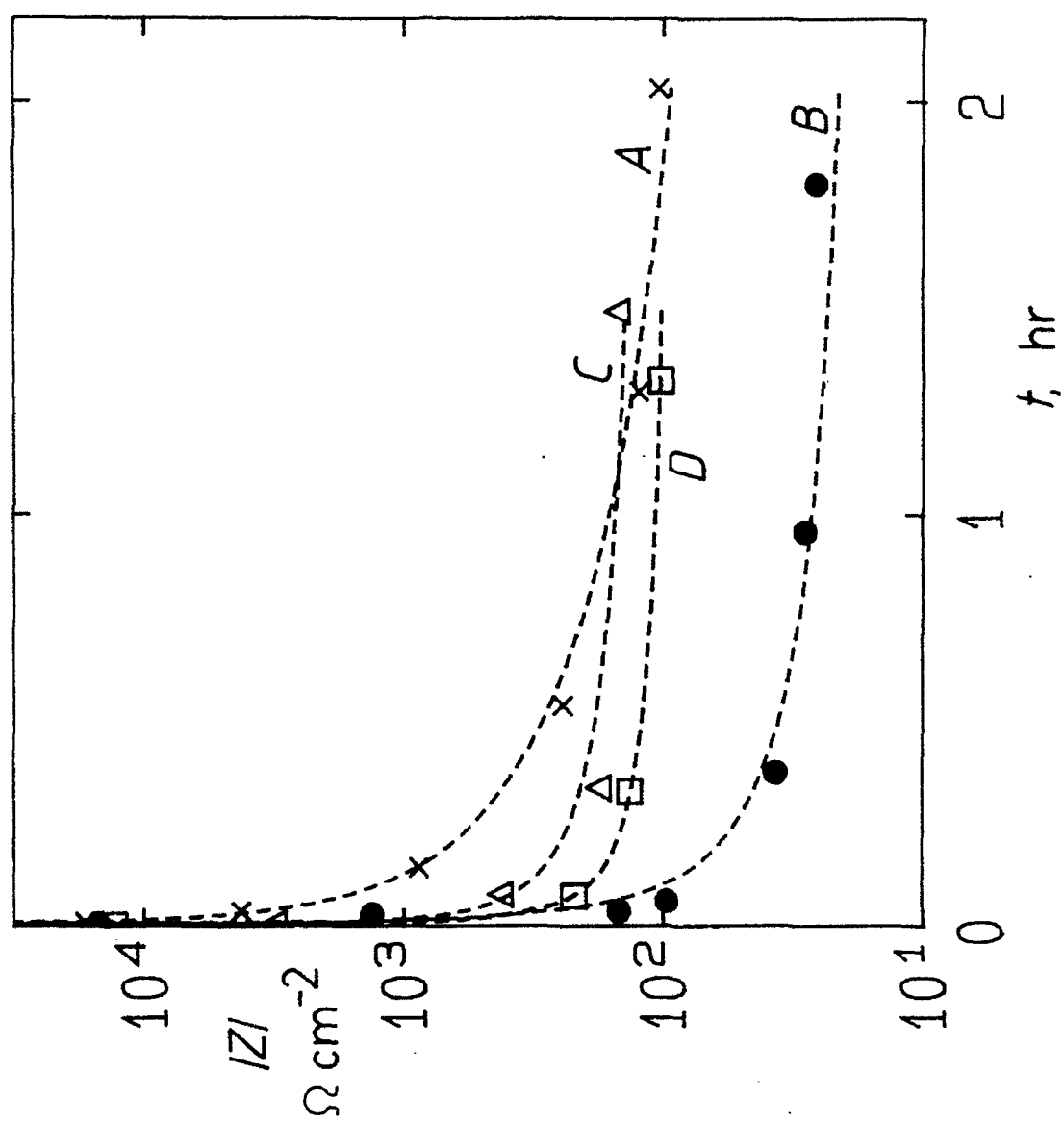
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Fig 1

Fig. 2

Fig. 3

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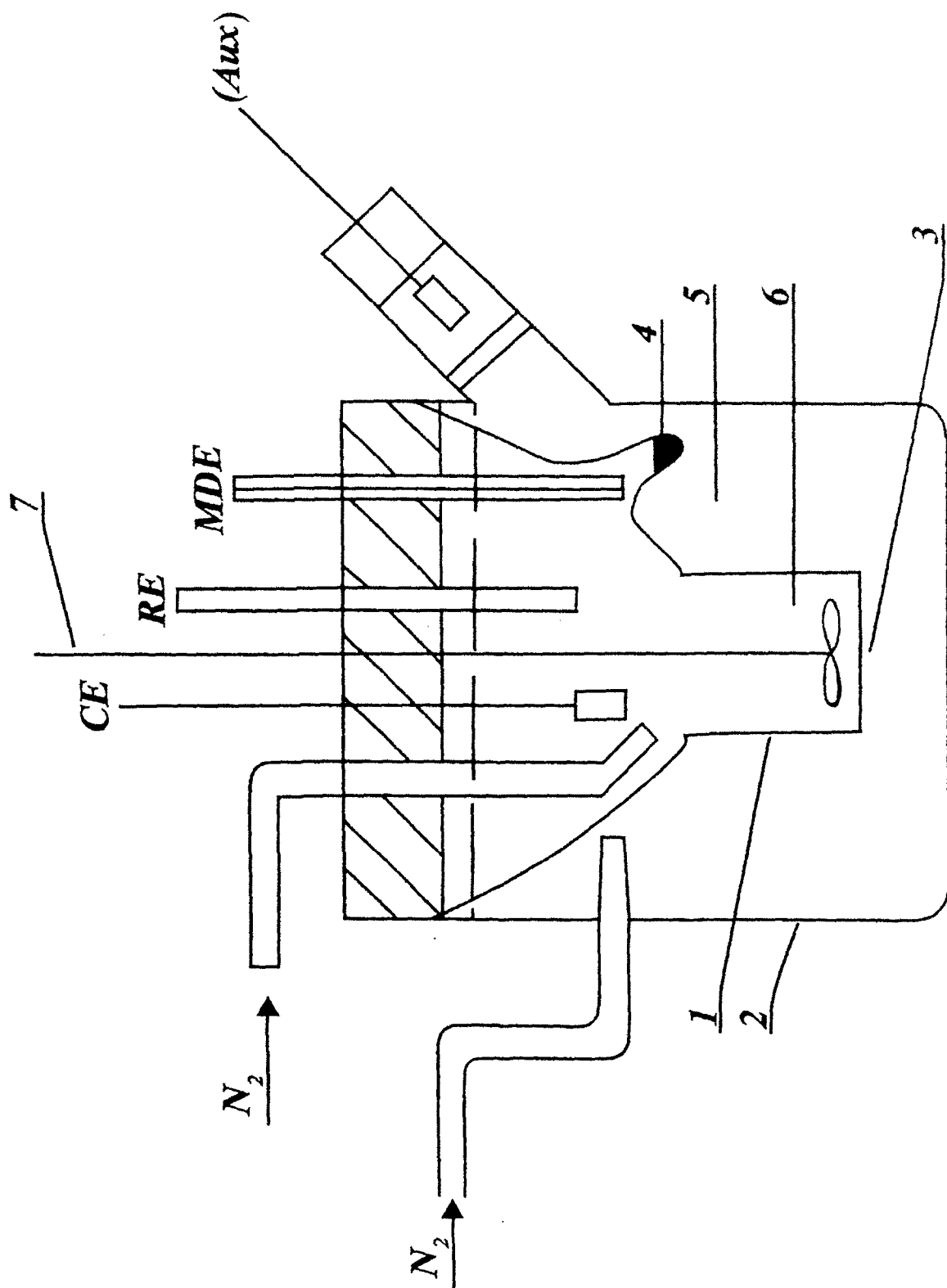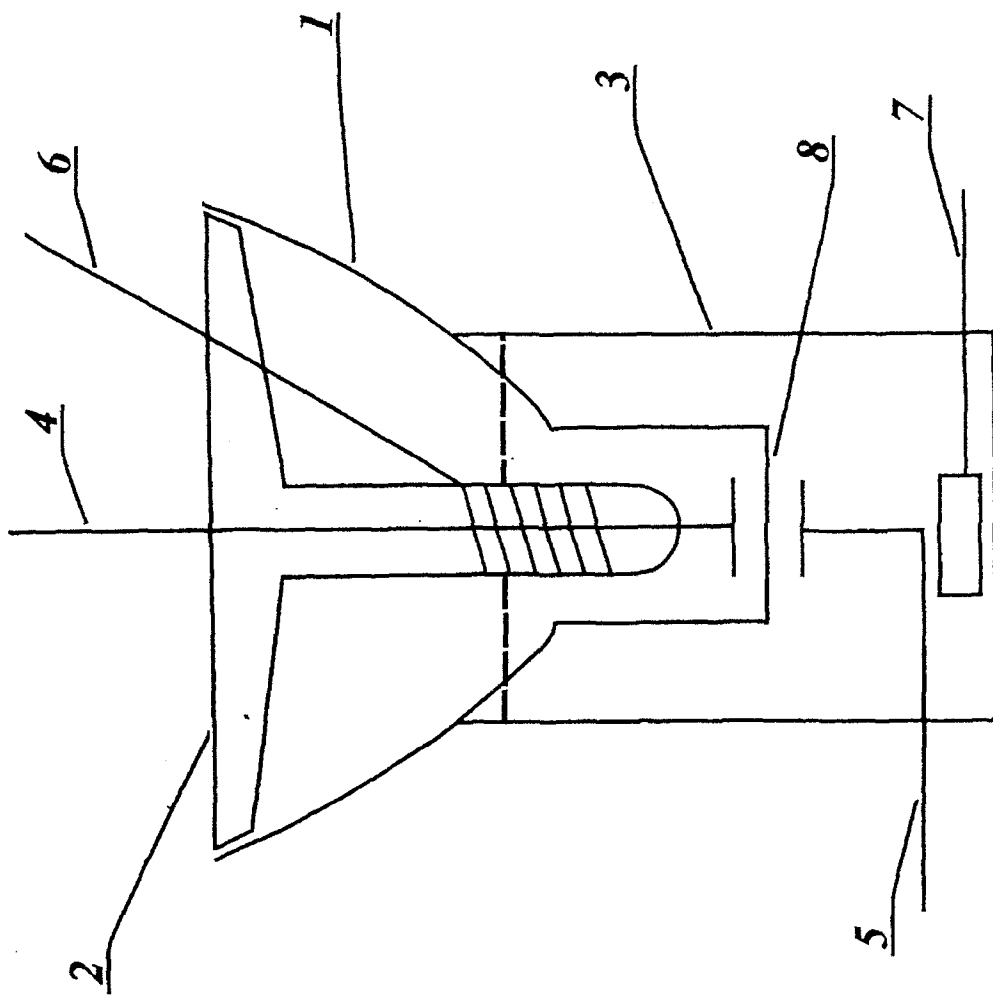
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